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# Kinetics and Thermodynamics of the CN Molecule. I. Decomposition Mechanism for CN Molecules

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Two different reaction mechanisms,

 $CN+CN\rightarrow C_2+N_2$ 

and also

 $CN+M\rightarrow C+N+M$ ,

have been reported for the decomposition of CN molecules behind shock waves. The current analytical study demonstrates that these two observed mechanisms are special cases of the generally applicable CN decomposition chain,

 $CN+M\rightarrow C+N+M$ ,  $C+CN\rightarrow C_2+N$ ,  $N+CN\rightarrow N_2+C$ ,

in which the first reaction or a combination of the second and third reactions can dominate, depending on temperature and CN concentration.

or

#### I. INTRODUCTION

The formation and decomposition of CN molecules behind shock waves have been studied by several investigators. Bauer *et al.*<sup>1</sup> measured the rate of formation of CN from  $C_2N_2$  in Ar mixtures, while Patterson and Greene<sup>2</sup> measured the rate of formation of CN from BrCN-Ar mixtures. Knight and Rink<sup>3</sup> monitored the density behind shock waves in  $C_2N_2$ -Kr mixtures and determined the rate of CN formation. In each of these studies, the mechanism for CN formation from either  $C_2N_2$  or BrCN was observed to be a bimolecular reaction involving the diluent gas. However, studies of the decomposition of CN molecules behind shock waves have led to two reported mechanisms. Patterson and Greene<sup>2</sup> and Fairbairn<sup>4</sup> observed that CN molecules decompose according to the mechanism

$$2CN \rightarrow C_2 + N_2, \tag{1}$$

over the range  $T = 3400-7000^{\circ}$ K. Recently, Fairbairn<sup>5</sup> observed that the following mechanism is responsible for the decay of CN molecules:

$$CN+M \rightarrow C+N+M, \qquad (2)$$

over the range  $T = 7000-15\ 000^{\circ}$ K, where M is the argon diluent. The rate data obtained by these studies<sup>2,4,5</sup> are shown in Fig. 1.

#### **II. DECOMPOSITION MECHANISM**

The current study was undertaken to demonstrate that the two different reaction mechanisms observed are special cases of the following more general CN decomposition mechanism first suggested by Fairbairn<sup>5</sup>:

$$BrCN+M \rightleftharpoons Br+CN+M$$
 (3)

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 $C_2N_2 + M \rightleftharpoons CN + CN + M,$  (3')

$$CN + M \rightleftharpoons C + N + M, \tag{4}$$

$$CN+C \rightleftharpoons C_2+N,$$
 (5)

$$CN+N \rightleftharpoons N_2+C,$$
 (6)

$$C_2 + M \rightleftharpoons C + C + M, \tag{7}$$

$$N_2 + M \rightleftharpoons N + N + M. \tag{8}$$

Note that Reactions (5) and (6) are stoichiometrically equivalent to Reaction (1) and that Reaction (1) may be excluded since it is not an *a priori* requirement for the experimentally observed production of  $C_2$ . For the above reaction chain, the rate of decay of CN molecules is governed by Eqs. (4)–(6) and can be written

$$-\frac{d[CN]}{dt} = k_4[M][CN] \left(1 + \frac{k_5}{k_4} \frac{[C]}{[M]} + \frac{k_6}{k_4} \frac{[N]}{[M]}\right)$$
$$-\frac{k_4[C][N][M]}{K_4} \left(1 + \frac{k_5K_4[C_2]}{k_4K_5[C][M]} + \frac{k_6K_4[N_2]}{k_4K_6[N][M]}\right),$$
(9)

where k is the forward rate coefficient, K is the equilibrium constant, and the subscripts correspond to the particular reactions. At conditions far from equilibrium, such as the peak CN concentration behind a shock wave, the second term of Eq. (9) can be neglected, giving

$$-d[\mathrm{CN}]/dt = k_4[\mathrm{M}][\mathrm{CN}](1+F), \qquad (10)$$

$$F = \frac{k_5}{k_4} \frac{[\text{C}]}{[\text{M}]} + \frac{k_6}{k_4} \frac{[\text{N}]}{[\text{M}]}.$$

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded t IP: 129 174 21 5 On: Sat. 20 Dec 2014 19:03:37 If  $F \ll 1$ , the decay of CN molecules will appear to be governed by Reaction (4). Alternatively, for  $F \gg 1$ , the decay of CN molecules will be governed by Reactions (5) and (6), but will have the over-all appearance of Reaction (1). The function F can vary significantly for changes in temperature which will affect the rate coefficients and for different initial mixture ratios which will affect [C]/[M] and [N]/[M].

## III. EVALUATION OF F

To test this complex reaction model, F was evaluated at experimental conditions typical of the CN decompo-



FIG. 1. CN decomposition reaction rate coefficients.

sition experiments.<sup>2,5</sup> The earlier work of Fairbairn<sup>4</sup> was excluded because of the relatively limited data available from this source. Evaluation of F required the concentration of C and N, which were obtained by numerical integration (fourth-order Runge-Kutta) of the full rate equations corresponding to Reactions (3)-(8), to obtain the time-dependent concentrations of all species involved. The rate coefficients used in this integration are listed in Table I, and their selection is discussed separately in the Appendix. The concentrations of C and N atoms used in function F were either those at 5  $\mu$ sec (particle time) behind the shock front (the earliest observable time following the transit of a shock front across a window slit) or at the peak of the CN concentration if this occurs later. The values of Fobtained are listed in Table II together with the corresponding experimental conditions.

For the conditions of Fairbairn's<sup>5</sup> experiment,

TABLE I. Selected reaction rates.

Reaction	Rate coefficient $(cc^n mole^{-n} \cdot sec^{-1})^n$	Ref.
(3)	$k_D = 2.0 \times 10^{12} T^{1/2} \exp(-90 \ 500/RT)$	2
(3')	$k_D = 1.15 \times 10^{10} T^{1/2} (125 \ 000/RT)^{5.5} \times \exp(-125 \ 000/RT)$	1
(4)	$k_D = 1.2 \times 10^{14} \exp(-71 \ 000/T)$	5
(5)	$k_D = 4 \times 10^{13}$	•••
(6)	$k_D = 4 \times 10^{13}$	•••
(7)	$k_R = 2.0 \times 10^{15}$	7
(8)	$k_R = 8.3 \times 10^{19} T^{-1.6}$	6

<sup>a</sup>  $k_D$  is the forward or dissociation rate coefficient, and  $k_R$  is the backward or recombination rate coefficient.

Reaction (4) dominates since F < 1 [see Eq. (10)], while at Patterson's experimental conditions Reactions (5) and (6) dominate since F > 1. Hence, this analysis, involving a common over-all reaction mechanism, agrees with the observations of the two CN decomposition experiments.

By changing the order of magnitude of the rate coefficients for Reactions (5) and (6), the function F changes about an order of magnitude in the same direction. To ascertain that the original selection of the rate coefficients was indeed not fortuitous, the computed CN and C<sub>2</sub> profiles were compared with published experimental emission profiles at about 8000°K. Figure 2 shows that the perturbed rate coefficients neither reproduced the experimental CN decay nor the plateau of the C<sub>2</sub> profile, while good qualitative agreement was obtained with the original selected rate coefficients. Note that agreement would not be epected in the first 5  $\mu$ sec (particle time) because of the shock transit time across the window slits and the finite rise time of the sensors. Furthermore, experimental CN and C2 emission profiles obtained by Patterson<sup>2</sup> at about 7750°K were in reasonable agreement with the concentration profiles predicted with the selected rate coefficients of Table I (see Fig. 3). This

 
 TABLE II. The function F computed for various experimental conditions.

Reference to which conditions apply	BrCN (mole %)	Т <sub>2</sub> (°К)	P <sub>1</sub> (mm Hg)	F
5	0.1	7 700	10	0.8
5	0.1	10 000	10	0.5
5	0.1	10 000	1	0.068
5	0.025	10 000	1	0.016
2	5.0	7 700	1	4.7
2	1.0	7 700	1	1.6
2	5.0	5 500	10	50.0
2	1.0	5 500	10	26.0
2	5.0	5 500	1	70.0



FIG. 2 (a) Computed CN concentration and experimental CN emission (Ref. 5) behind shock wave; 0.1% BrCN in argon;  $P_1 = 10$  torr;  $U_s = 2.85$  mm/ $\mu$ sec. (b) Computed C<sub>2</sub> concentration and experimental C<sub>2</sub> emission (Ref. 5) behind shock wave; 0.1% BrCN in argon;  $P_1 = 10$  torr;  $U_s = 2.85$  mm/ $\mu$ sec.



FIG. 3. Computed concentrations and experimental emission (Ref. 2) for CN and C<sub>2</sub> behind shock wave; 5% BrCN in argon;  $P_1 = 1.0$  torr;  $U_s = 2.92$  mm/µsec.

agreement between experimental profiles and the predicted profiles justifies the original selection of the rate coefficients for Reactions (5) and (6) and confirms that the values of F given in Table II are sufficiently accurate to indicate the dominant CN decomposition reactions.

By making small adjustments in the rate coefficients, better agreement could be obtained between the experimental and computed profiles in Figs. 2 and 3. Considering the uncertainties in the experimentally established rates, the nonidealities of attenuation and boundary layer growth in the tube, and the uncertain relation between observed emission and the groundstate concentration, it was not considered profitable to make small adjustments to the selected rates in Table I. However, it can be argued (see Appendix) that  $k_6$  should be considerably greater than  $k_5$ . Therefore several cases were examined in which  $k_5$  and  $k_6$ were varied within the limits of an order-of-magnitude decrease and increase, respectively, from the original common value of  $4 \times 10^{13}$  cc mole<sup>-1</sup> · sec<sup>-1</sup>. The function F did not change significantly from the values given in Table II, and for  $k_5 = 2 \times 10^{13}$  and  $k_6 = 2 \times 10^{14}$  cc mole<sup>-1</sup>·sec<sup>-1</sup> equally good agreement was obtained between the computed CN and C<sub>2</sub> concentrations and the experimental data in Figs. 2 and 3.

## IV. CONCLUSIONS

We have shown that the decomposition of CN molecules apparently follows the reaction chain given by Reactions (4)-(6). The observations of Fairbairn<sup>5</sup> represent a special case in which Reaction (4) dominates, while the observations of Patterson<sup>2</sup> represent the other case in which Reactions (5) and (6) dominate, giving the appearance of Reaction (1). We are currently conducting additional shock-tube studies of CN decomposition in our laboratory. A wide range of temperature and mixture ratio is being investigated to substantiate further the decomposition mechanism and to obtain rate coefficients for Reactions (5)-(7).

## **APPENDIX: SELECTION OF RATE COEFFICIENTS**

The rate coefficients for Reactions (3), (3'), (4), and (8), given in Table I, have been determined experimentally.<sup>1,2,5,6</sup> Fairbairn<sup>7</sup> estimated that the upper limit for the dissociation rate of  $C_2$  in Reaction (7)

lies between  $3.1 \times 10^{11}$  and  $9.5 \times 10^{11}$  cc mole<sup>-1</sup>·sec<sup>-1</sup> at 8000°K. A lower limit for this same reaction can be obtained from the published results of Patterson.<sup>2</sup> Figure 1(b) of that reference shows the decay of  $C_2^*(0, 0)$  radiation at about 7500°K, and by using Patterson's analytical technique,<sup>2</sup> the rate coefficient for the dissociation of C<sub>2</sub> was estimated as  $k_7 = 1.1 \times$  $10^{11}$  cc mole<sup>-1</sup>·sec<sup>-1</sup>. This is a lower bound because the effect of Reaction (5) was neglected, but nonetheless the rate coefficient has been bracketed in the region  $1.1 \times 10^{11} \le k_7 \le 9.5 \times 10^{11}$  cc mole<sup>-1</sup> sec<sup>-1</sup> at about 8000°K. Variation with temperature was incorporated by converting  $k_7$  to a recombination rate (independent of temperature) and using the equilibrium relation to define the dissociation coefficient. No rate data on Reactions (5) and (6) are available. A survey of similar bimolecular exchange reactions has shown that the forward rates are mainly of order 10<sup>13</sup> cc mole<sup>-1</sup>·sec<sup>-1</sup> and are almost independent of temperature. The rates for Reactions (5) and (6) were therefore assumed equal, and the values in Table I were primarily influenced by the known rates for  $O+CN\rightarrow N+CO^{8}$ NO+CN $\rightarrow$ N<sub>2</sub>+CO,<sup>8</sup> and H+HBr $\rightarrow$ H<sub>2</sub>+Br.<sup>9</sup>

The assumption that  $k_5 = k_6$  is questionable since the net energy changes associated with these reactions are approximately<sup>10,11</sup>  $\Delta E_5 = +34$  and  $\Delta E_6 = -47$  kcal/mole, which suggests that  $k_6$  would be considerably greater than  $k_5$ . To demonstrate that the results for  $k_5 = k_6$ are nonetheless valid, several cases were examined with  $k_6 > k_5$ , and these are discussed in Sec. III.

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